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Synthesis and evaluation of a novel fluorescent sensor based on hexahomotrioxacalix[3]arene for Zn^{2+} and Cd^{2+}

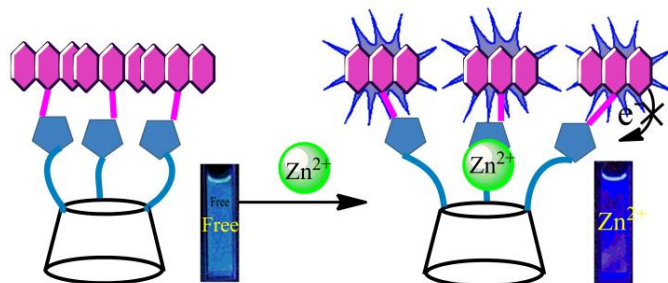
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1. Introduction

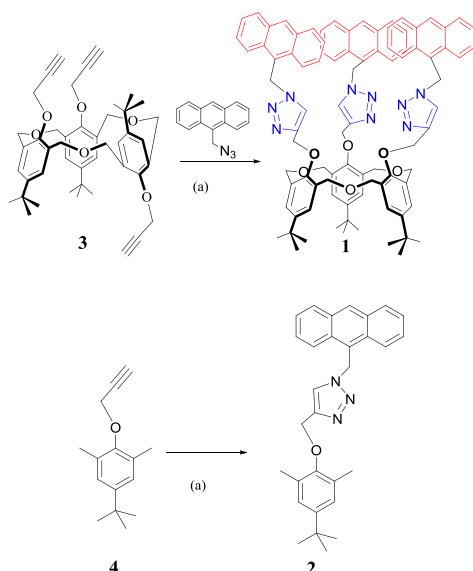
Owing to their simplicity, high sensitivity, and low detection limits for trace chemicals in chemistry, biology, and the environment,^{1,2} fluorescent chemosensors have received much attention in the field of supramolecular chemistry. Generally, an effective fluorescent chemosensor consists of an ion recognition unit and a fluorogenic unit, which converts the actuating signal from the ionophore unit into a light signal. Amongst the different fluorogenic units, anthracene derivatives are key species in the design of fluorescent chemosensors materials, which have found wide utilization in lasers, phosphors, and light-emitting devices.³ Although a tremendous number of anthracene-based organic materials have been investigated with the aim of potential applications as photoluminescence (PL) and/or electroluminescence (EL) devices in films and the solid state, the practical development of PL and EL devices is in fact restricted, usually owing to their poor stability. In contrast, strongly luminescent anthracene-based inorganic–organic hybrid materials with higher stability could be a class of promising candidates for light-emitting as well as EL applications.⁴

Calixarenes and their derivatives are attractive compounds for use in host–guest and supramolecular chemistry. In particular,

hexahomotrioxacalix[3]arene derivatives with C_3 -symmetry can selectively bind ammonium ions which play important roles in both chemistry and biology.^{5,6} Furthermore, the incorporation of two types of recognition sites via the introduction of different ionophores on the hexahomotrioxacalix[3]arene will create potential heteroditopic receptors with the capability of binding cations and anions, *e.g.* ammonium ions and halides. Therefore, many fluorescent chemosensors based on calixarenes, which show highly selective recognition of metal cations,⁷ ammonium cations,⁸ and fullerene derivatives, have been reported.⁹

Additionally, the use of Click chemistry¹⁰ has seen a significant growth in the derivatization of calixarenes owing to its reliability, specificity, biocompatibility, and efficiency. It has been proven to be a promising strategy for the chemical modification of calixarenes. In 2005, Zhao and co-workers¹¹ applied Click chemistry to the synthesis of water soluble calixarenes, which laid a solid foundation for this methodology. Click chemistry has also been used to synthesize calixarene conjugates of chromophores and bioactive molecules such as glycosides,¹² sialoclasters,¹³ and amino acids.¹⁴ Because of the highly selective nature of the alkyne-azide cycloaddition, the Click reaction is a general method to introduce various functional groups/moieties at the upper or lower rim of calixarenes. Therefore, we hypothesized that suitably arranged functionalized groups containing nitrogen atoms attached to a hexahomotrioxacalix[3]arene should be a good receptor candidate

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Scheme 1. Synthetic pathway for compounds **1** and **2**. (a) CuI in THF and water, reflux, 20 h.

for cations. Therefore, with this in mind, we have synthesized chemosensor **1** and studied its cation-binding affinity.

2. Results and discussion

The synthesis of **1** was carried out as shown in Scheme 1. We first synthesized **3** in 55 % yield by the reaction of hexahomotrioxacalix[3]arene and propargyl bromide in the presence of Cs_2CO_3 in dry acetone solution. The ^1H NMR spectroscopic results suggested that **3** adopts a *partial-cone* structure.¹⁵ Accordingly, fluorescent compound **1** can be obtained from the reaction of **3** with 9-azidomethylanthracene under standard conditions for Click chemistry. The coupling of **3** with 9-azidomethylanthracene afforded *cone* conformation compound **1** in 75 % yield. ^1H NMR spectrum of **1** shows a singlet for the *tert*-butyl protons at δ 0.94 ppm, and a doublet at δ 4.03 ppm for the bridge protons, and ^{13}C NMR spectrum of **1** exhibits two peaks for the methyl and the quaternary carbon atoms of the *t*-Bu groups at δ 31.32, 34.04 ppm, three peaks for methylene carbon at 45.51, 66.94, 68.87 ppm and 14 peaks for aromatic carbon, respectively, indicating a C_3 -symmetric structure for sensor **1**. The same procedure was also employed in the synthesis of **2** from 4-*tert*-butyl-2,6-dimethylphenol (Scheme 1). Compound **1** contains both the calixarene and the triazole groups as metal ion binding sites, whereas **2** contains only a triazole for metal ion binding. Compare to compound **1**, ^1H NMR spectrum of the reference compound **2** shows that the protons on the anthracene ring appeared at the lower magnetic fields at around δ 7.52–8.60 ppm ($\Delta\delta$ 0.05–0.2 ppm), and the proton on the triazole ring also appeared at the lower magnetic field at δ 7.08 ppm ($\Delta\delta$ 0.11 ppm) (Fig. S23). These findings strongly indicate the anthracene moieties appended on **1** were sterically-fixed to be in close proximity to allow the formation of π - π stacking between the anthracene moieties.

Solutions giving concentrations of **1** (10 μM) in CH_3CN were prepared as follows. Test solutions were prepared by taking 70 mL of the calixarene stock solution in a 10 mL volumetric flask, adding 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mL of stock solution, and making up to the volume with CH_3CN . The fluorescence spectrum of **1** (10 μM) in CH_3CN exhibits a characteristic monomer emission of anthracene. The fluorescence emission of the solutions was measured at an excitation wavelength of 365 nm, and the emission intensities were

measured at 418 nm. Measurements were repeated a minimum of three times for each addition. At high concentrations, emission quenching was observed, suggesting the formation of intermolecular associates of **1**.

However, under dilute conditions, emission quenching was not observed. The critical association concentration value determined from the concentration-variable emission spectra was determined to be 10 μM . To remove effects of the inter-molecular associates, absorption and fluorescence measurements were carried out under critical association concentration. A similar procedure for the fluorescence measurements of **2** was conducted. The fluorescence emission of the solutions was measured at an excitation wavelength of 365 nm, and the emission intensities were measured at 418 nm. More interestingly, compared to **2**, the fluorescence intensity of **1** is obviously different from reference compound **2** at the concentration (30 μM). The fluorescence spectra of **1** and **2** under the same solutions are shown in Fig. 1. When **2** was excited at 365 nm, strong emission peaks near 400–500 nm were observed, which were assigned as emission from single anthracene moiety, respectively. In contrast, when **1** was excited at 365 nm, the emission peaks were weak. These observations indicated that the formation of π - π stacking between the anthracene moieties appended on **1** can quench the fluorescence.

To get an insight into the binding properties of chemosensor **1** toward metal cations, we first investigated the fluorescence changes upon addition of a wide range of metal cations including K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Cr^{3+} , Fe^{2+} , Ni^{2+} , Sr^{2+} , Ag^+ , Hg^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} ,

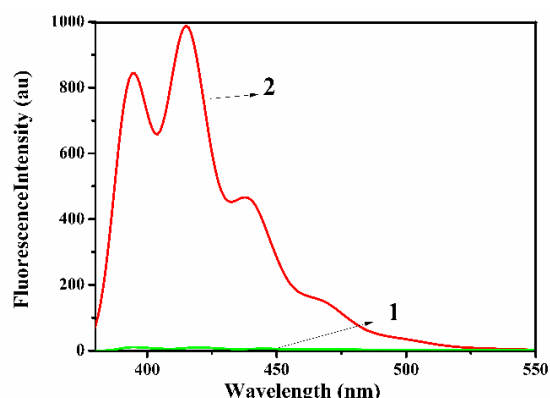


Fig. 1. Fluorescence spectra of **1** (10 μM) and **2** (30 μM) in CH_3CN .

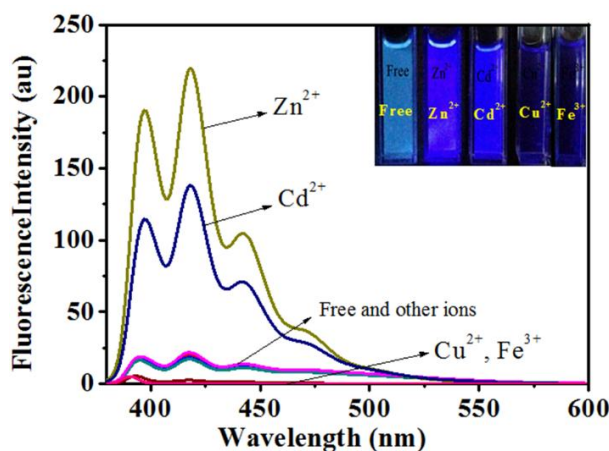


Fig. 2. Fluorescence spectra of **1** (10 μM) in CH_3CN in the presence of different metal ions (10 equiv.). Metal ions include K^+ , Na^+ , Li^+ , Ca^{2+} , Cr^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Fe^{3+} , Fe^{2+} and Pb^{2+} . Excitation was performed at 365 nm.

Zn²⁺ and Cd²⁺. The fluorescence changes are depicted in Fig. 2 and Fig. 3. Addition of Zn²⁺ and Cd²⁺ to the solution of **1** induced obvious ratiometric changes, where the emission increases. By contrast, no significant spectral changes were observed upon addition of most of the other metal cations apart from Cu²⁺ and Fe³⁺ where quenching was observed. These results suggest that complexations between **1** and Cu²⁺, Fe³⁺, Zn²⁺ and Cd²⁺ ions through intermolecular interaction might be proposed.

In contrast to chemosensor **1**, chemosensor **2** exhibited a strong emission at 418 nm, and similar experiment was carried out. The fluorescence intensity changes of **2** upon addition of different metal ions are shown in Fig. S3. Addition of Cu²⁺ and Fe³⁺ caused a strong and medium fluorescence quenching, respectively.

Upon addition of Zn²⁺, the fluorescence intensity of solution **1** increased gradually (Fig. 4). The saturation behavior of the fluorescence intensity after adding 2 equivalents of Zn²⁺ reveals that a 1:1 stoichiometry best describes the binding mode of Zn²⁺ and **1**, which is also supported by the Job's plot data (Fig. S6). According to the 1:1 model, the association constant of Zn²⁺, calculated from the Benesi-Hildebrand equation,¹⁶ was found to be $1.44 \times 10^4 \text{ M}^{-1}$. As a result, **1** can be regarded as being highly sensitive to the Zn²⁺ ion, especially given the large fluorescence dynamic range and the low detection limit of $3.79 \times 10^{-7} \text{ M}$. The quantum yield of **1** is $\Phi = 0.11$.

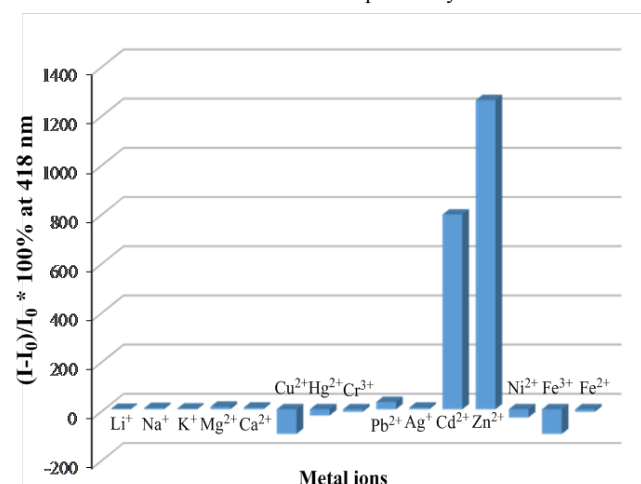


Fig. 3. Fluorescence responses of receptor **1** (10 μM) to 100 μM various tested ions in CH_3CN . I_0 is the fluorescence emission intensity at 418 nm for free receptor **1**, and I is the fluorescent intensity after adding ions at 298 K. $\lambda_{\text{ex}} = 365 \text{ nm}$.

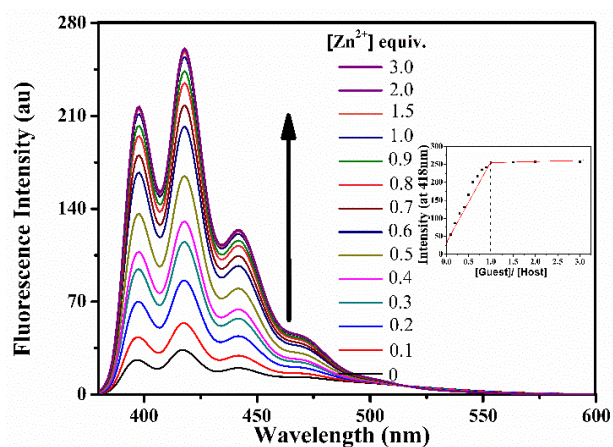


Fig. 4. Changes in fluorescence emission spectra of **1** (10 μM) upon titration by Zn²⁺ (from 0 – 30 μM) in CH_3CN (excitation at 365 nm). Inset is molar ratio plot.

To further study the sensitivity of **1** toward Cd²⁺, fluorescence titration experiments were carried out (Fig. 5). Upon addition of Cd²⁺, the fluorescence intensity of solution **1** increased gradually. A Job's plot binding between **1** and Cd²⁺ ion reveals a 1:1 stoichiometry (Fig. S10), while the association constant (K_a value) for the complexation with Cd²⁺ ion by **1** was determined to be $4.06 \times 10^4 \text{ M}^{-1}$ as observed by the fluorescence titration experiments in CH_3CN . On the other hand, the fluorescence of **1** was efficiently quenched by Cu²⁺ and Fe³⁺; over 99 % fluorescence quenching was observed with 10 equiv. A Job's plot binding between **1** and Cu²⁺ ion reveals a 1:1 stoichiometry (Fig. S15), while the association constant of Cu²⁺, calculated from the Benesi-Hildebrand equation,¹⁶ was found to be $5.79 \times 10^5 \text{ M}^{-1}$.

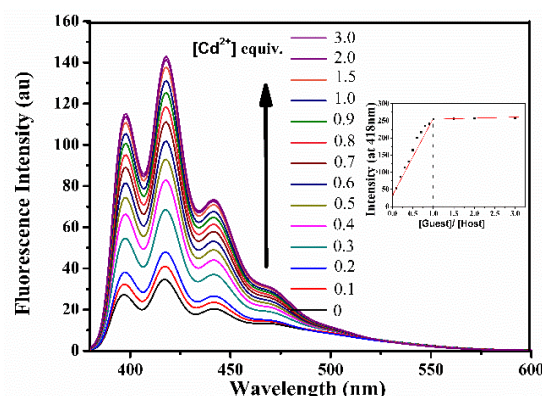


Fig. 5. Changes in fluorescence emission spectra of **1** (10 μM) upon titration by Cd²⁺ (from 0 – 30 μM) in CH_3CN (excitation at 365 nm). Inset is molar ratio plot.

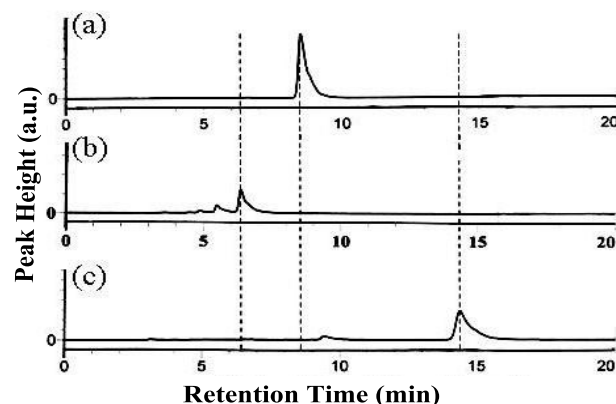


Fig. 6. HPLC chromatograms of derivative **1** and complex (a) 0.3 mM of **1**; (b) 0.3 mM of **1** with 6 mM of Cu²⁺ is added; (c) 0.3 mM of **1** with 6 mM of Zn²⁺ is added.

The compound **1**, **1**•Cu²⁺ and **1**•Zn²⁺ mixtures were also analyzed by HPLC (Fig. 6). A chromatographic peak of derivative **1** appeared at 8.40 min. After the addition of Cu²⁺ and Zn²⁺, the intensity of the peak at 8.40 min decreased, accompanied by the emergence of a new peaks at 6.30 min and 14.50 min, respectively; these results demonstrate clearly the formation of new products (**1**•Cu²⁺ and **1**•Zn²⁺ complexes).

To confirm the binding mechanism, ¹H NMR spectra of the **1** and **1**•Zn²⁺ complex were measured in a mixture of $\text{CDCl}_3/\text{CD}_3\text{CN}$ (10:1, v/v). As shown in Fig. 7B, upon gradual addition of Zn²⁺ salt (0.5 equiv.) to a solution of **1**, the resonances corresponding to the protons of receptor **1** were split into two sets of signals. After addition of 1 equiv. Zn²⁺ in receptor **1** the original proton signals

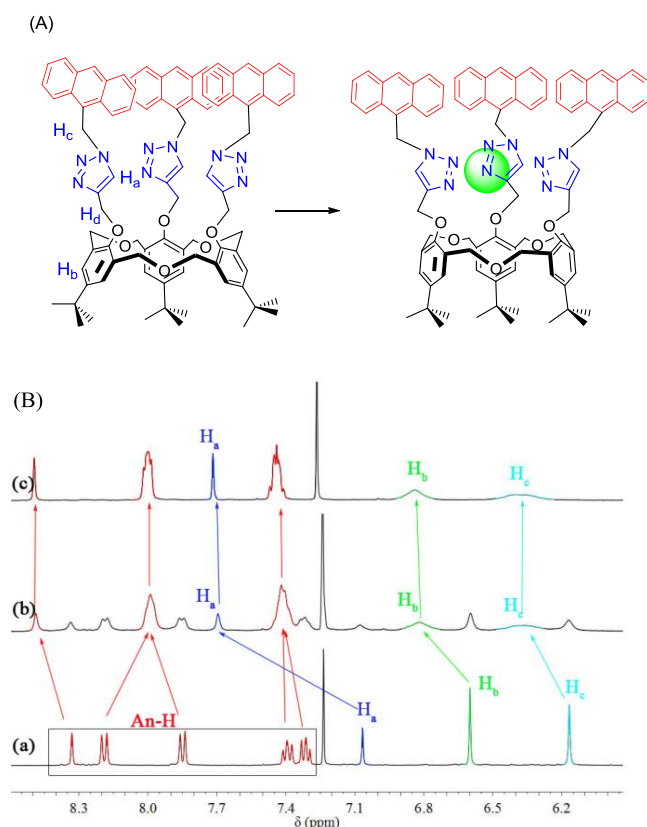


Fig. 7. (A) Binding mode of **1** upon complexation with Zn²⁺ ion as perchlorate salt. (B) Partial ¹H NMR spectra of **1** (4.0 mM) in CDCl₃:CD₃CN (10:1, v/v) upon addition of Zn²⁺ ion at 298 K. (a) Free **1**, (b) **1** + Zn²⁺ (0.5 equiv.), and (c) **1** + Zn²⁺ (1.0 equiv.).

disappeared. This result suggests the presence of the complexed form between **1** + Zn²⁺ and the uncomplexed form of free **1**. The signal for proton H_a on the triazole ring undergoes a downfield shift from δ 7.16 ppm to 7.70 ppm ($\Delta\delta_{\text{H}} = 0.64$ ppm), and the OCH₂-triazole linked proton of H_d is shifted from δ 4.06 ppm to 5.13 ppm (Fig. S22). These spectral changes suggested that the Zn²⁺ ion is selectively bound by the nitrogen atoms on the triazole rings. Moreover, the signal for the proton on the anthracene moiety revealed a down-field shift, which indicated that the anthracene moieties appended on **1** were alienated by Zn²⁺ to prohibit the formation of π - π stacking between the anthracene moiety. On the other hand, it is noted that the proton H_b on the phenyl of hexahomotrioxacalix[3]arene also experienced a downfield shift from δ 6.60 to 6.81 ppm, and the $\Delta\delta_{\text{H}}$ value for H_{ax} and H_{eq} of the ArCH₂O methylene protons changed to 0.58 ppm (Fig. S22), respectively. The large $\Delta\delta_{\text{H}}$ value for H_{ax} and H_{eq} indicated that the phenol groups in the complex are positioned in a more-upright form, the calix cavity changed from a "flattened-cone" to a more-upright form that is similar to the previously reported examples.^{17,18} The concept of Zn²⁺ complexation by the host chemosensor **1** is shown in Fig. 7A. From this above discussion, the binding mode of **1**•Zn²⁺ explore that the phenol groups in the complex are situated as an upright form and also the anthracene moieties are far apart from each other to reduce the π - π stacking in presence of Zn²⁺ which results the fluorescence enhancement.

On the other hand, the peaks of H_a, H_b, H_c and H_d completely disappeared and the signals of the anthracene ring protons and benzyl protons were blurred, which attributed to both the conformation changes and the paramagnetic effect of the Cu²⁺. Once the Cu²⁺ was captured by the nitrogen, the protons adjacent to Cu²⁺ were strongly affected by the Cu²⁺ due to inherent paramagnetism of

Cu²⁺. Thus, the complexation between the heavy metal ions and sensor **1** led to the quenching of the fluorescence emission through the heavy metal ion effect, and/or the reversed PET that is similar to the previously reported examples.¹⁹

3. Conclusions

In summary, we have synthesized a new type of selective and sensitive fluorescent sensor having triazole rings as the binding sites at the lower rim of a hexahomotrioxacalix[3]arene scaffold in a cone conformation. The selective binding behaviour of chemosensor **1** has been evaluated by fluorescence spectra and ¹H NMR spectroscopic analysis. This sensor has desirable properties for practical applications, including selectivity for detecting Zn²⁺ and Cd²⁺ in the presence of excess competing metal ions at low ion concentration or as a fluorescence enhancement type chemosensor due to the cavity of calixarene changed from a "flattened-cone" to a more-upright form and inhibition of photoinduced electron transfer (PET). In contrast, the results suggested that receptor **1** is highly sensitive and selective for Cu²⁺ and Fe³⁺ as a fluorescence quenching type chemosensor due to the photoinduced electron transfer (PET) or heavy atom effect.

Further studies on the synthesis of tritopic receptors based on the hexahomotrioxacalix[3]arene are also underway in our laboratory.

4. Experimental section

4.1. General

All melting points (Yanagimoto MP-S1) are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and Varian-400MR-vnmrs400 with SiMe₄ as AQ2OM spectrophotometer. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance mass spectrometer at 75 eV by using a direct-inlet system. UV-vis spectra were recorded using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Elemental analyses were performed by a Yanaco MT-5. Fluorescence quantum yields were recorded in solution (Hamamatsu Photonics K. K. Quantaurus-QY A10094) using the integrated sphere absolute PL quantum yield measurement method.

4.2. Materials

Compounds **3** and **4** were synthesized according to our previous report.¹⁵

4.2.1. Synthesis of receptor 1. Copper iodide (20 mg) was added to a solution of compound **3** (200 mg, 0.28 mmol) and 9-azidomethylanthracene (210 mg, 0.90 mmol) in 20 mL THF/H₂O (4:1) and the mixture was heated at 65 °C for 24 h. The resulting solution was cooled and diluted with water and extracted thrice with CH₂Cl₂. The organic layer was separated and dried (MgSO₄) and evaporated to give the solid crude product. The residue was eluted from a column chromatography of silica gel with hexane/ethyl acetate (v/v = 4:1) to give the desired product cone-**1** (290 mg, 75 %) as colorless prisms. Mp 154–156 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.94 (27H, s, C(CH₃)₃), 4.03 (12H, d, OCH₂O, $J = 4.0$ Hz), 4.10 (6H, s, -OCH₂), 6.29 (6H, s, An-CH₂), 6.68 (6H, s, Ar-H), 7.08 (3H, s, triazole-H), 7.39–7.43 (6H, m, An-H), 7.47–7.51 (6H, m, An-H), 7.94 (6H, d, $J = 8.4$ Hz, An-H), 8.28 (6H, d, $J = 8.4$ Hz, An-H) and 8.42 (3H, s, An-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 31.32, 34.12, 45.51, 66.94, 68.87, 122.71, 123.29, 124.42, 125.45, 125.77, 127.64, 129.42, 129.74, 130.77, 130.86, 131.43, 144.27, 146.23 and 151.78 ppm. IR: ν_{max} (KBr)/cm⁻¹: 3310, 2960, 1575, 1436, 1367, 1268, 1090 and 1002. FABMS: m/z : 1389.58 (M⁺). Anal. Calcd for C₉₀H₈₇O₆N₉ (1389.12): C, 77.73; H, 6.31. Found: C, 77.90; H, 6.37.

4.2.2. Synthesis of receptor 2. Copper iodide (20 mg) was added to a

solution of compound **4** (100 mg, 0.47 mmol) and 9-azidomethylanthracene (340 mg, 1.45 mmol) in 20 mL THF/H₂O (4:1) and the mixture was heated at 65 °C for 24 h. The resulting solution was cooled and diluted with water and extracted thrice with CH₂Cl₂. The organic layer was separated and dried (MgSO₄) and evaporated to give the solid crude product. The residue was eluted from a column chromatography of silica gel with hexane/ethyl acetate (v/v = 4:1) to give the desired product **2** (170 mg, 81 %) as colorless prisms. Mp 194–196 °C. ¹H NMR (300 MHz, CDCl₃) δ 1.22 (s, 9H, C(CH₃)₃), 2.10 (s, 6H, Ar-CH₃), 4.78 (s, 2H, -OCH₂), 6.57 (s, 2H, An-CH₂), 6.89 (s, 2H, Ar-H), 7.19 (s, 1H, trizole-H), 7.52–7.64 (m, 4H, An-H), 8.09 (d, 2H, J = 6.0 Hz, An-H), 8.33 (d, 2H, J = 6.0 Hz, An-H), 8.60 (s, 1H, An-H). ¹³C NMR (CDCl₃, 75 MHz, CDCl₃): δ 31.6, 34.2, 37.4, 46.7, 49.85, 62.2, 114.3, 122.5, 123.1, 123.8, 125.6, 126.3, 127.9, 129.7, 130.1, 130.9, 131.6, 144.0, 144.5, 156.0. IR: ν_{max} (KBr)/cm⁻¹: 3019, 1966. FABMS: m/z: 449.78 (M⁺). Anal. Calcd for C₃₀H₃₁ON₃ (449.25): C, 80.14; H, 6.95. Found: C, 80.38; H, 7.03.

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Supplementary data

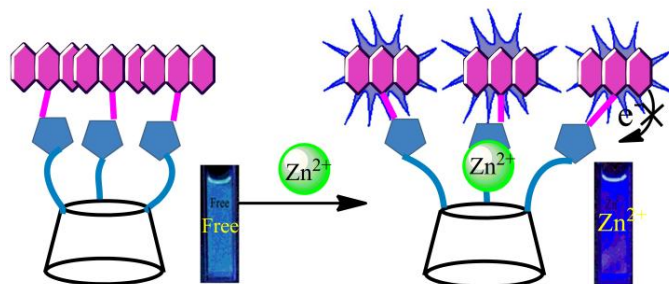
Supplementary data (Details of the NMR spectra and titration experimental data) associated with this article can be found in the online version, at XXXXX.

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Synthesis and evaluation of a novel fluorescent sensor based on hexahomotrioxacalix[3]arene for Zn^{2+} and Cd^{2+}

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